Short communication

Extraction of pesticides using supercritical trifluoromethane and carbon dioxide

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Abstract

The off-line supercritical fluid extraction of pesticides using trifluoromethane (CHF_3) and carbon dioxide (CO_2) is described. Pesticides containing nitrogen or phosphorus heteroatoms were used as analytes to determine the extraction ability of CHF_3 in comparison with CO_2 at various pressures and densities. A 15% increase in extraction efficiency was obtained when CHF_3 was used as the extraction solvent rather than CO_2. No selectivity was observed for different groups of pesticides, although CHF_3 has a dipole moment whereas CO_2 does not. Because in environmental matrices the hydrocarbons are mostly present in high excess compared with the pesticides, extractions were carried out without and with addition of alkanes and polycyclic aromatic hydrocarbons (PAHs). The extraction efficiency of the pesticides with CHF_3 performed without addition of alkanes and PAHs was significantly decreased.

1. Introduction

An attractive alternative to conventional liquid solvent extraction for the recovery of organic analytes from adsorbents and solids is analytical-scale supercritical fluid extraction (SFE). Owing to the physical properties of supercritical fluids (SCFs), i.e., higher diffusion coefficients than liquids and high solubility, the extraction is fast and high recoveries are obtained. Many researchers have reported the use of supercritical carbon dioxide to extract various pollutants, e.g., polychlorinated biphenyls (PCBs), polycyclic aromatic hydrocarbons (PAHs) and pesticides, from different matrices such as soil, sediments and biological material [1–13]. The solvation power of pure carbon dioxide, which is the most often used SCF, is limited to apolar or slightly polar compounds even at very high densities. Therefore, SFE of polar analytes requires the addition of organic polarity modifiers to CO_2, mostly methanol, to enhance the solvation power and the mobile phase selectivity [14–18].

Another method for extracting polar analytes from solid matrices is the reaction of derivatizing reagents with the analyte under supercritical conditions [19,20]. Hills et al. [21] investigated simultaneous supercritical fluid derivatization and extraction (SFDE) using silylation reagents for the extraction of roasted coffee beans, tea and marine sediment. They found that a silylation reagent not only served as a derivatizing reagent but also acted as a coextracting reagent,

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which increased the extraction yield of medium-polarity compounds [22]. In situ chemical derivatizations of 2,4-D from soil, of phenols from C_{18} sorbent discs and of fatty acids from whole cells using trimethylphenylammonium hydroxide and boron trifluoride in methanol have been reported by Hawthorne et al. [23]. An on-line supercritical fluid derivatization and extraction procedure coupled with capillary gas chromatography was performed by Hillmann and Bächmann [24] to extract phenoxycarboxylic acids from a C_{18} sorbent and to eliminate excess of derivatizing reagent by fractionated SFE. On-line SFDE was used by King et al. [25] to determine the fatty acid composition of oilseeds.

Many investigators have used alternative fluids to overcome the limited solvation power of non-polar CO_2 and the problems presented by mixed mobile phase systems [26–28]. Hawthorne et al. [29] compared the SFE recoveries for native pollutants including PCBs from a standard reference material and PAHs from a petroleum waste sludge and from a railroad bed using supercritical $CHClF_2$, N_2O and CO_2. Sulfur hexafluoride (SF_6), nitrous oxide and SF_6-modified carbon dioxide were used in on-line SFE–GC to characterize complex environmental and petroleum matrices [30].

The use of trifluoromethane (CHF_3) as a supercritical fluid for extracting polar analytes, has several advantages over $CHClF_2$, which has a comparable polarity. CHF_3 has a lower critical temperature and a less harmful environmental effect than $CHClF_2$. Howard et al. [31] evaluated the use of CHF_3 to extract sulfonylurea herbicides, which are polar and thermally labile, from Celite and PAHs from filter-paper and clay.

This paper describes the comparison of the SFE rates obtained for the off-line extraction of polar pesticides at the low ppm level from silanized glass beads using CHF_3 and CO_2. Different classes of pesticides, i.e., triazines, organophosphorus compounds, carbamates and anilides, were used as analytes. The effect of pressure and density of the fluids on extractability and the addition of alkanes and PAHs to the inert, non-adsorptive matrix is described.

2. Experimental

2.1. Reagents

The pesticides used, atrazine, desethylatrazine, diazinon, fenpropimorph, malathion, metazachlor, metribuzine, propiconazol and triallate (CAS numbers 1912-24-9, –, 333-41-5, 67564-91-4, 121-75-5, 67129-08-2, 21087-64-9, 60207-90-1, 006-039-00-X) were supplied by Riedel-de Haën (Seelze, Germany). Chrysene, pyrene, benzo-[ghi]perylene, dodecane, tetradecane and hexadecane were purchased from Supelco (Deisenhofen, Germany). Solutions of the pesticides were prepared at 200 μg/ml each in acetone. The solutions of the PAHs and the alkanes had concentrations of 200 and 250 μg/ml, respectively, in acetone.

2.2. Off-line SFE

Extractions with CHF_3 (Linde, Unterschleissheim, Germany; purity of 99.999%) were performed using a Milton Roy (Riviera Beach, FL, USA) Model CP3000 cryogenically cooled (6°C) dual-head reciprocating pump. Extractions with CO_2 (Messer Griesheim, Frankfurt, Germany; supplied in a cylinder with a dip tube, purity of 99.9995%) were performed using a computer-controlled, high-pressure syringe pump (Series 600; Lee Scientific, Salt Lake City, UT, USA). The SFE pumps were connected to the extraction cell with 1/16 in. O.D. stainless-steel tubing and finger-tight Dynaseal connectors (Knauer, Berlin, Germany). Extraction cells were placed inside a Sichromat II-GC oven (Siemens, Karlsruhe, Germany) to maintain the extraction temperature. Extraction cells with internal volumes of 120 μl were filled with silanized glass beads and spiked with 5 μl of the pesticide solution. The solvent was allowed to evaporate for 10 min. Fused-silica tubing (SGE, Weiterstadt, Germany) of 25 μm I.D. was used to control SFE flow-rates at 100–200 ml gaseous carbon dioxide and trifluoromethane, respectively, depending on the operating pressure. The extracted analytes and the supercritical fluid

were collected by inserting the outlet end of the restrictor into empty vials, which were designed for the concentration of liquid samples (6-ml volume). The vials were cryogenically cooled with liquid nitrogen during extraction. The end of the restrictor was heated with a resistance heater to avoid clogging of the restrictor. At the end of the extraction, the resistance heater was shut off and the vial was removed from the liquid nitrogen. After venting the carbon dioxide or the trifluoromethane at room temperature, the analytes were dissolved in 200 μl of acetone and analysed without further steps.

2.3. GC instrumentation

The extracted pesticides were analysed using a Model 5890 Series II gas chromatograph (Hewlett-Packard, Bad Homburg, Germany) with nitrogen–phosphorus detection (NPD). The split–splitless injector and the detector were operated at 250 and 280°C, respectively. The pesticides were separated on a 50 m × 0.25 mm I.D. SE-54 column (Macherey–Nagel, Düren, Germany) with a film thickness of 0.25 μm. The carrier gas was helium at an initial linear velocity of 40 cm/s. The column oven temperature was held at 100°C for 1 min, then programmed at 10°C/min to 150°C and at 5°C/min to 290°C.

3. Results and discussion

The aim of this investigation was to compare the extraction abilities of two different fluids, CHF_3, and CO_2. Trifluoromethane was selected because it has nearly the same critical temperature as CO_2 and because of its analogous structure to chloroform, which is a good organic solvent and is capable of hydrogen bonding. The comparison of the extraction abilities, which are an indication of the solubility of the pesticides, was carried out at constant temperature in order to remove the effect of vapour pressure.

The analytes used were nitrogen- and phosphorus-containing pesticides, some of which

show good water solubility and therefore harmful environmental effects in ground water. They are widely used in agriculture and the European Community Drinking Water Directive sets a limit of 0.1 μg/l for individual pesticides and 0.5 μg/l for the sum of all pesticides.

The trapping efficiency of the collection unit was investigated in an earlier study with C_8–C_{16} n-alkanes [9] and found to be quantitative. During extraction the collection vials were cryogenically cooled with liquid nitrogen. Because of the very low vapour pressures of the selected pesticides (between 10^{-4} and 10^{-7} hPa at 20°C) compared with n-octane (15 hPa at 20°C) and their polarity, the trapping efficiency in this investigation was assumed to be quantitative. The reproducibility of all extractions for the standard solutions was between 2% and 9% (n = 3). Table 1 summarizes the pressure dependence of the extractability of the selected pesticides from silanized glass beads with supercritical CHF_3 at a constant temperature. Only the extraction profiles for atrazine, fenpropimorph, and diazinon under various extraction conditions are shown in Fig. 1 because those for the other

Table 1
Effect of pressure on the recovery (%) of pesticides from glass beads by SFE using CHF_3

Analyte	Pressure (MPa)[a]			
	13.8	20.7	28.0	34.5
Desethylatrazine	72.9	96.5	68.5	84.0
Atrazine	78.4	95.4	63.6	70.8
Diazinon	69.4	86.5	62.5	61.7
Triallate	72.8	84.5	61.2	66.7
Metribuzine	77.4	94.6	66.2	64.2
Malathion	73.5	92.2	66.1	64.7
Fenpropimorph	66.7	84.3	71.3	75.6
Metazachlor	72.5	86.3	60.8	72.6
Propiconazol	64.6	87.7	73.6	76.5

The R.S.D.s (n = 3) for all percentage recoveries were between 2% and 9%.
[a] Conditions: extraction temperature = 26°C; extraction time = 30 min; matrix = silanized glass beads; trap temperature = liquid nitrogen temperature; extraction vessel size = 120 μl.
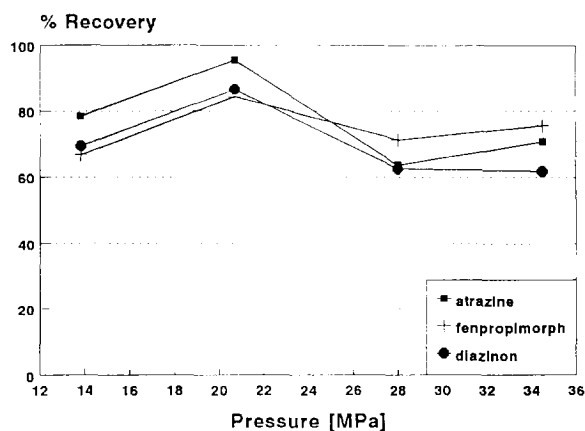
% Recovery

Fig. 1. Effect of pressure on the extraction of (■) atrazine, (+) fenpropimorph and (●) diazinon from silanized glass beads at 26°C and with an extraction time of 30 min. Percentage recoveries are based on those reported for CHF₃ extractions in Table 1.

pesticides differed in the total recovery, but not in the profile. At the lowest pressure the extractibility for most pesticides is greater than 72%, which is acceptable for multi-component analysis [32]. It can be seen that at pressures >20 MPa (i.e., reduced pressure >4) the recovery slopes down again for all pesticides. This phenomenon can be described as a consequence of repulsive forces "squeezing" the solute out of solution [33]. This investigation showed no selectivity for the different groups of pesticides if they were extracted with CHF_3 at 26°C and various pressures.

Tables 2 and 3 give the results obtained following the extraction at various densities with trifluoromethane and carbon dioxide. The temperature and the extraction time were kept constant at 50°C and 15 min, respectively, for both supercritical fluids during extraction. The highest recoveries for all the pesticides except for triallate and fenpropimorph were found at a density of 0.8 g/ml for both supercritical fluids. The reduced density and therefore the pressure needed to obtain this density was lower for CHF_3 than CO_2 because of the higher density and lower pressure of CHF_3 at its critical point. Fig. 2 shows as an example the extraction profiles for atrazine at various reduced densities

Table 2
Effects of density on the recovery (%) of the pesticides from glass beads by SFE using CHF_3

Analyte	Density (g/ml)[a]			
	0.6	0.7	0.8	0.9
Desethylatrazine	72.8	72.0	77.9	66.7
Atrazine	80.8	75.0	91.8	60.8
Diazinon	68.0	67.4	73.3	48.1
Triallate	73.3	71.0	70.7	55.8
Metribuzine	77.2	72.0	86.8	59.0
Malathion	75.1	71.4	82.1	55.0
Fenpropimorph	67.8	77.3	61.1	57.2
Metazachlor	69.9	72.7	78.4	57.6
Propiconazol	48.1	72.0	76.6	57.8

The R.S.D.s ($n = 3$) for all percentage recoveries were between 2% and 9%.
[a] Conditions: extraction temperature = 50°C; extraction time = 15 min; matrix = silanized glass beads; trap temperature = liquid nitrogen temperature; extraction vessel size = 120 μl.

because the extraction profiles for the other pesticides differed only in total recovery. No selectivity could be observed for different groups of pesticides, e.g., the polar triazines having aromatic amino groups and the less polar or-

Table 3
Effects of density on the recovery (%) of the pesticides from glass beads by SFE using CO_2

Analyte	Density (g/ml)[a]			
	0.6	0.7	0.8	0.9
Desethylatrazine	67.1	60.1	66.7	30.2
Atrazine	49.4	52.5	72.3	39.0
Diazinon	40.6	41.5	64.1	36.5
Triallate	41.5	44.8	65.7	34.6
Metribuzine	47.0	55.0	71.6	35.6
Malathion	47.4	45.9	70.2	40.1
Fenpropimorph	52.5	55.9	72.0	44.2
Metazachlor	50.0	58.1	66.3	38.8
Propiconazol	56.1	67.4	83.5	50.4

The R.S.D.s ($n = 3$) for all percentage recoveries were between 2% and 9%.
[a] Conditions: extraction temperature = 50°C; extraction time = 15 min; matrix = silanized glass beads; trap temperature = liquid nitrogen temperature; extraction vessel size = 120 μl.
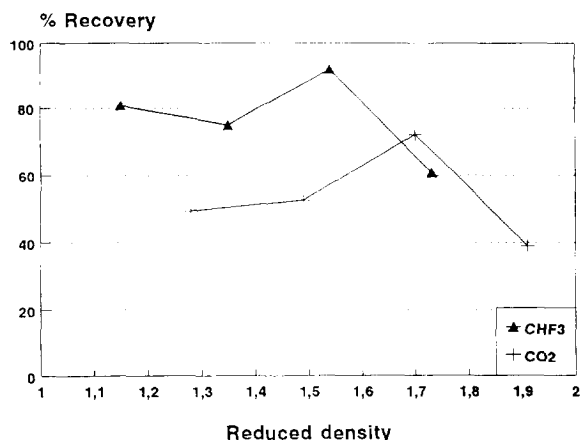
% Recovery

Fig. 2. Effect of the reduced density on the extraction of atrazine from silanized glass beads by SFE with (+) CO_2 versus (▲) CHF_3. Extractions were performed at 50°C for 15 min at densities of 0.6, 0.7, 0.8 and 0.9 g/ml for each supercritical fluid. Percentage recoveries are based on those reported for CHF_3 and CO_2 extractions in Tables 2 and 3, respectively.

Table 4
Recovery of pesticides from glass beads without addition of PAHs and alkanes by SFE using CHF_3

Analyte	Density (g/ml)[a]			
	0.6	0.7	0.8	0.9
Desethylatrazine	n.d.	60.1	66.7	30.2
Atrazine	19.2	52.5	72.3	39.0
Diazinon	16.4	41.5	64.1	36.5
Triallate	19.0	44.8	65.7	34.6
Metribuzine	18.9	55.0	71.6	35.6
Malathion	19.1	45.9	70.2	40.1
Fenpropimorph	17.2	55.9	72.0	44.2
Metazachlor	17.7	58.1	66.3	38.8
Propiconazol	15.0	67.4	83.5	50.4

The R.S.D.s ($n = 3$) for all percentage recoveries were between 2% and 9%.
[a] Conditions: extraction temperature = 50°C; extraction time = 15 min; matrix = silanized glass beads; trap temperature = liquid nitrogen temperature; extraction vessel size = 120 μl.

ganophosphorus insecticides, although CHF_3 is capable of hydrogen bonding and has a large dipole moment of 1.6 D whereas CO_2 is without a dipole moment.

Because in environmental matrices the hydrocarbons are mostly present in large excess compared with the pesticides, all previous extractions were performed with the addition of alkanes and PAHs. Table 4 lists the results observed following the extraction of the pesticides without an addition of alkanes and PAHs. They were compared with the results shown in Table 2. The extractions were performed using only CHF_3 at different densities because the use of this supercritical fluid yields higher recoveries in the previous investigations compared with CO_2. Fig. 3 shows as an example the extraction profiles for atrazine. It can be seen that the extraction ability of CHF_3 for the selected pesticides without addition of alkanes and PAHs was significantly decreased. It is assumed that the hydrocarbons act as modifiers whereby the polarizability of the supercritical fluid was increased because CHF_3 is a small, hard molecule with a large dipole moment. Dobbs et al. [34] noted that a non-polar modifier such as octane has the same effect on polar and non-polar solutes to increase their

solubility in a supercritical fluid if the molecular masses or polarizabilities are similar. In contrast, a polar modifier may increase markedly the solubility of a polar solute, but may not affect that of a non-polar solute. However, Schmitt and Reid [35] showed that fluoroform is a poor
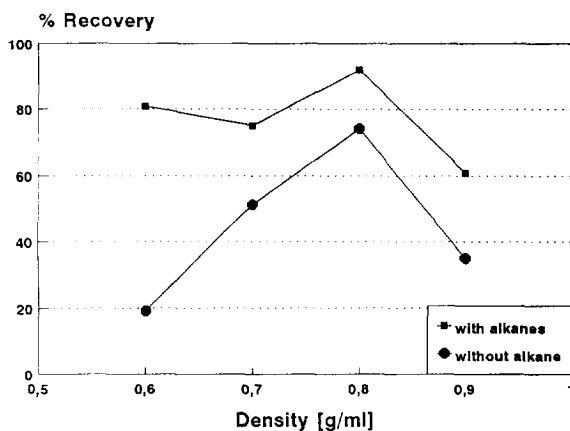
% Recovery

Fig. 3. Extractability of atrazine from silanized glass beads (■) with and (●) without PAHs and alkanes by SFE using CHF_3. SFE was performed at 50°C for 15 min. After additionally spiking the glass beads with 5 μl of the alkane/PAH solution, the solvent was allowed to evaporate for 10 min.

solvent for hydrocarbons, but found it to be a good solvent for molecules containing functional groups capable of hydrogen-bond association with the acid proton on fluoroform, such as carbonyl and amine.

4. Conclusions

The extraction of pesticides, i.e., triazines, organophosphorus insecticides, carbamates and anilides, using CHF_3 yields higher recoveries than CO_2 but the recoveries are not quantitative. No selectivity for pesticides of different polarity can be observed, although CHF_3 has a dipole moment whereas CO_2 does not. Extractions were carried out without and with the addition of alkanes and PAHs. The extraction efficiency of the pesticides with CHF_3 performed without the addition of alkanes and PAHs was significantly decreased.

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